

MTL TR 89-35

ADA208223

U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
ATTN: SLCMT-IML TECHNICAL LIBRARY DIVISION
WATERTOWN, MA. 02172-0001

CURRENT STATUS OF THE CARBON FIBER INDUSTRY IN JAPAN

SIN-SHONG LIN
MATERIALS SCIENCE BRANCH

April 1989

Approved for public release; distribution unlimited.



U.S. ARMY MATERIALS TECHNOLOGY LABORATORY
Watertown, Massachusetts 02172-0001

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

Mention of any trade names or manufacturers in this report shall not be construed as advertising nor as an official indorsement or approval of such products or companies by the United States Government.

DISPOSITION INSTRUCTIONS

Destroy this report when it is no longer needed.
Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER MTL TR 89-35	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CURRENT STATUS OF THE CARBON FIBER INDUSTRY IN JAPAN		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Sin-Shong Lin		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Army Materials Technology Laboratory, Watertown, Massachusetts 02172-0001 SLCMT-EMS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS D/A Project: 1L162105AH84 AMCMS Code: 612105.H840011
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, Maryland 20783-1145		12. REPORT DATE April 1989
		13. NUMBER OF PAGES 20
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES To be published in the Office of Naval Research, Far East Scientific Informa- tion Bulletin, v. 14, no. 2, Tokyo Office, 1989.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Carbon fiber Pitch-based carbon fiber PAN-based carbon fiber Processing of carbon fiber		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) (SEE REVERSE SIDE)		

two-thirds of the world production and consumes only one-third or less. Accordingly, in Japan much attention is focused on the progress and development (Ref 4,5) as well as the production of carbon fibers. The fabrication technology for PAN fiber was originally developed in Japan in 1958 (Ref 6) and has been improving steadily since then. Several large Japanese manufacturing corporations, such as Toray, Toho, Mitsubishi Rayon, and Kureha, are actively searching for alternative process improvements for higher strength fibers as well as expansion of material applications. The manufacturing process and technology of medium-grade PAN fibers are well established at this time as are production methods. The GP pitch-based fibers, which were first produced from isotropic pitches in 1970 (Ref 7,8), are commercially available for low-cost reinforcement of building materials. However, the HPCF pitch-based fibers produced from anisotropic or mesophase pitches are still in the developmental stage, although a few of the products are currently on the market.

Pitch-based carbon fiber is emerging as a material competitive with the PAN-based fiber in both performance and cost. The possibility of encroachment of the existing PAN fibers market by the new pitch-based fiber is the subject of many arguments and discussions (Ref 1). Regardless of the uncertainties in the future economic outlook, pitch-based fibers have several advantages that should not be ignored:

- (1) The fiber is a higher added value product made from the readily available low cost materials, petroleum pitch and coal tar.
- (2) It has excellent physical properties comparable to the PAN fibers.
- (3) The manufacturing processes are reported to be simpler than the processes for PAN fibers.
- (4) The future economic outlook is very optimistic based on market projections.

The two largest producers of PAN fibers, Toray and Toho Rayon, are located in Japan. The combined production capacity of both companies exceeds 3,000 tons per year, which is about 40 percent of the worldwide production (Ref 2). The total production of PAN fibers around the world is about 85 percent, and the remaining 15 percent or less is mostly general-purpose pitch-based fibers produced by Kureha Co., Mitsubishi Chemical Co., and Osaka Gas Co. Some high-grade pitch-based fibers are available from Mitsubishi Chemical, Kashima Oil, and Osaka Gas. In Japan there are over 25 companies actively engaged in the development of pitch-based carbon fibers, and their activities and progress have shown varying degrees of success. Although most of the companies are not yet in the production stage, their research efforts are expected to produce a breakthrough in the low-cost processing technology for high-performance fibers.

OVERVIEW OF MANUFACTURING PROCESSES

The basic process for manufacturing CF (Ref 9-11) consists of a series of steps involving: (1) precursor preparation,

CURRENT STATUS OF THE CARBON FIBER INDUSTRY IN JAPAN

Sin-Shong Lin

The information contained in this report was gathered during a 7-week trip to the Far East as part of the expanded mission of the Army Material Technology Laboratory (MTL) to survey recent developments and advances in carbon fibers. Carbon fibers are known to play a significant role in fiber-reinforced materials for lightweight structures and other high-performance applications. Increasing applications are expected in many types of aerospace and commercial components in the near future. In this article, a brief description of the carbon fiber manufacturing process is given, followed by recent efforts of the Japanese carbon fiber industries, such as current status, progress, research highlights, and process development. Some relevant technical problems and possible improvements of the fiber process are discussed.

INTRODUCTION

There is a wide variety of available carbon fibers. Generally, commercially available carbon fibers (CF) in Japan can be grouped into polyacrylonitrile (PAN) and pitch-based fibers based on the precursor materials, either polyacrylonitrile or petroleum pitch/coal tar. The commercial PAN-based fibers usually have medium to high tensile strengths, while the pitch-based fibers tend to have high tensile modulus. This distinction is becoming less valid due to the availability of the medium-high modulus grade PAN fibers. The pitch-based CF currently available are further divided into general-purpose (GP) grade, usually short

fibers of lower mechanical strength, and high-performance (HPCF) grade, fibers with excellent mechanical properties comparable to the high-quality PAN fibers. Furthermore, according to the mechanical strength, the fibers are grouped into high tensile strength (HT), high modulus (HM), ultra high modulus (UHM), and high elongation. The commercial applications of these fibers are quite different based on their physical and mechanical properties. The PAN-based fibers are used mainly in lightweight structural components such as aircraft secondary frames and leisure products. The GP fibers are used widely in high-temperature insulating materials, reinforcements for engineering plastics, carbon materials and concrete, and as an alternative to asbestos. But for HPCF, the major applications are in the fabrication of advanced composite materials for aerospace equipment based on the material strength, rigidity, electric, and other properties. Also some applications are in the carbon/carbon (C/C) composite materials for rocket components based on unique high-temperature properties.

The worldwide consumption (Ref 1-3) of all carbon fibers, including high-performance and general-purpose PAN- and pitch-based fibers, exceeded 7,500 tons in 1987 (Ref 2), of which more than 85 percent are PAN-based fibers. The demand is expected to increase due to the development of many new applications, especially in the field of fiber-reinforced concretes, fiber-reinforced plastics, and other structural reinforcement utilizations. Of worldwide demand, Japan produces

gradual stage or in multiple stages is a necessary production procedure. Copolymerization with vinyl chloride or with other polymers to promote complete carbonization and preferred orientation is the subject of ongoing research efforts. The average molecular weight as well as the molecular weight distribution are also considered in the final formation of the PAN polymer filaments. The control of variation in the average molecular weight of copolymers can improve the mechanical strength or the physical characteristics of the resulting CF. Since modification of the precursor polymer chemistry greatly affects the processing parameters, research is focused on the modifications within the limit of the current production technology.

Pitch-Based Carbon Fibers

Pitch is a mixture of condensed aromatic hydrocarbon with or without alkyl branches, and conventional pitches show no optical anisotropy. The molecular weight of an individual pitch unit varies widely and may be in the range of 300 to 4,000. Thus pitch usually has a molecular weight distribution depending on the source and the processing condition. Accordingly, the pitch constituents can be grouped into benzene, quinoline, and pyridine soluble/insoluble components (Ref 13).

For the production of GPCF the precursor is isotropic pitch, which contains a wide variety and range of molecular structures and is usually less pure. However, the HPCF precursor is anisotropic pitch so that fibers with highly oriented crystallites can be obtained during the spinning process.

When feed pitch is heated to remove low molecular weight volatile components, larger polynuclear aromatic compounds are formed. Around 400°C, the melt starts to separate into two phases. One phase appears as spherule and grows larger with increasing temperature. This phase is optically anisotropic and is the so-called mesophase. The second phase is the remaining isotropic melt. This anisotropic mesophase consists of large planar polynuclear aromatic molecules aligned together by weak Van der Waals forces, and it has a higher density than the surrounding isotropic phase. Gradually the anisotropic phase will aggregate by gravity sedimentation. If these two phases are separated, the anisotropic mesophase can be used as a starting raw material for HPCF.

After de-ashing, if necessary, the isotropic phase can be spun into filaments (GPCF) of low tensile strength and modulus. A slightly higher mechanical strength of the fiber can be obtained if a better isotropic pitch, either of a larger average molecular weight or a high purity precursor, is used.

The pitch obtained after direct heating is hard to process into fiber because: (1) the viscosity is too high at the softening temperature for easy spinning; (2) the condensation to larger molecules (infusible matter) and gas evolution continue at this temperature; and (3) two phases, anisotropic mesophase and isotropic matrix, exist together, making it difficult to process into fibers. The process used by Union Carbide Co. (AMOCO Co. now) is a modified method of direct heating. An additional agitation mechanism is incorporated into the spinning process to homogenize the two-phase pitch (Ref 13).

(2) spinning, (3) thermosetting, (4) carbonization, (5) graphitization, and two additional processes of (6) surface treatment and (7) epoxy sizing (Ref 12). However, the procedures involved in the processing are proprietary and are not released by the manufacturers.

In the PAN CF process, a special polyacrylonitrile copolymer fiber is stretched to align the polymer chains parallel to the fiber axis, and these linear backbones are converted into ribbons of continuous hexagonal carbon rings by oxidation (stabilization). This type of fiber has a sufficiently high glass transition temperature so that part of the orientation is retained after a carbonization cycle to 1,000 °C. Most elements other than carbon are removed during the combustion. The evolution of gases such as CH_4 , CO_2 , H_2O , NO , and a trace of HCN is observed. The orientation of the ribbons is further improved by heating to higher temperatures (carbonization or graphitization temperatures), which increase the modulus of the fiber. The conversion yield is less than 50 percent.

For the pitch-based CF, the precursor is a purified fraction of coal tar or petroleum pitch containing a large amount of liquid crystals or mesophases. In the process of melt spinning, the sheet-like aromatic hydrocarbons are easily oriented parallel to the fiber direction. The fibers are made infusible by oxidation (stabilization) and then carbonized, followed by graphitization. The crystallites in the pitch fiber are usually larger and better aligned than those in the PAN fiber and are oriented like strips of ribbon running along the fiber length. Consequently, the mesophase pitch fiber yields a high modulus. The conversion yield of pitch fiber is more than 90 percent.

PRECURSOR MATERIALS

PAN-Based Carbon Fibers

Specially processed polymer fiber is currently used for industrial production. The constituents of the fiber are somewhat different from the fibers used in textile fabrics in that the coloring, sizing, lustering, antistatic, and brightening compounds are absent. Additional chemicals are added to the polymer fiber to facilitate the stabilization and carbonization processes at the later stages. The starting PAN precursor contains at least 90 percent acrylonitrile units copolymerized with chemicals such as methylacrylate, methylmethacrylate, vinyl chloride, or vinyl acetate to achieve different molecular configurations. The additives can be divided into categories based on the objectives. Organic or inorganic phosphorous or halogen containing compounds are coated mainly to prevent excessive oxidation during the stabilization process. Aromatic compounds to aid fiber crystallinity and preferred orientation during the manufacturing process are also used. Precursor fibers without excessive macrovoids and with minimum micropores are highly preferable. Since the precursor composition is a prime factor in the final mechanical strength of the synthesized CF, manufacturers tend to follow their own proprietary formulations.

The preferred alignment and orientation of the polymer molecules along the fiber direction are a prime concern in the production of the precursor fiber. To improve the alignment in the polymer structure, the as-spun PAN fibers are frequently stretched by 100 to 500 percent at about 100 °C. Also during the carbonization process, the tensile stretching in either a single,

The current trend of the investigations is to find the best pitch composition that will provide easy spinnability and incorporate high mechanical strength into the resulting spun fibers. Thus, control of the spinning temperature and the precursor composition become very critical. From research efforts to improve the feed pitch composition, the present methods of attempting to narrow down the molecular weight distribution width of precursor pitch alone are not sufficient to obtain the optimum mechanical strength of CF. In order to manipulate fiber microstructure and to promote crystallite orientations, it seems necessary to create an entirely different composition of the feed pitch, such as two-pitch components (either anisotropic or isotropic) with varying softening points and molecular weight distributions. Perhaps an admixture of a second organic compound to promote perfect crystallization and preferred orientation for co-carbonization might improve the characteristics of the resulting spun fibers. Blendings of anthracene para-xylene-glycol (PXG), polyvinyl chloride (PVC) pitch, condensed polynuclear aromatic compounds (COPNA), AlCl_3 catalyst, and two-phase pitch have been experimentally tested (Ref 18-21). The roles of the additives are to: (1) act as a solvent to decrease the pitch viscosity, (2) react with feed pitch to modify condensation and aggregation processes by new reaction intermediates, and (3) promote sol polymerization reaction. If the microstructure and the surface morphology of the fibers could be controlled and manipulated, crack propagation, which is often initiated from surface flaws, would be retarded and reflected. Hopefully, the highest CF strength would be obtained.

SPINNING AND MICROSTRUCTURE CONTROL

In melt spinning pitch-based CF, the spinnability is the most important factor governing the filament drawing process. Since the softening temperature of the precursor pitch is 300 °C or more, the process has to be performed at a temperature 20 to 30 degrees higher. Thus, the proper viscosity is absolutely required for easy spinning. Spinning at higher temperatures accelerates degradation and aggregation of pitch molecules, producing infusible residues. Spinning at lower temperature and at a high viscosity produces discontinuous filaments.

It has been shown (Ref 17) that spinning at temperatures below or near the transition temperature of viscosity (T_v) tends to yield fiber with a radial type cross section (Figure 2). At a spinning temperature 50 °C or more above the transition temperature, a fiber cross section with an onion-type arrangement (Figure 3b) will be produced. In the intermediate temperature range, random or mosaic cross sections or mixtures of these patterns are formed (Figures 3a and 3c). The two pitches shown in the figure are hydrogenated in the autoclave either by THQ and hydrotreated anthracene oil (HAO) or by hydrogen gas in the presences of quinoline/anthracene solvents and catalysts (iron oxide, red mud, Co-Mo-alumina, or Ni-Mo-alumina) followed by heat treatment above 450 °C at a reduced pressure or inert gas bubbling. The viscosity transition temperature depends on the compositions as well as the sources of feed pitches.

There are several methods (Figure 1) to separate or to generate anisotropic mesophase from the raw materials, petroleum pitch or coal tar. The methods currently in use are hydrogen treatment with tetrahydroquinoline (THQ) (Kyushu Ind. Res.) (Ref 14) or with hydrogenated anthracene oil and catalyst (Nippon Petroleum) (Ref 15), thermal decomposition followed by gravity sedimentation (Toa Nenryo) (Ref 16), and the combination of heat treatment and solvent fractionation or hydrogenation (Ref 15). The basic principle involved in the above processes is to obtain a narrow molecular weight distribution of feed pitch in order to improve the

crystalline size and the crystal orientation of the spun fiber. Words such as pre-, neo-, and dormant mesophases are often used to describe the final pitch compositions after the treatments as shown in Figure 1. The Kyushu method yielded a feeding pitch (premesophase) that was isotropic but became anisotropic after spinning. The spinnability or the softening point of pitch must be considered in the choice of the feed pitch composition. The best choice of pitch composition (Ref 17) is: (1) melting point between 240 and 300 °C, (2) 80 to 95 wt. % of benzene insoluble and 10 to 40 wt. % of quinoline insoluble, and (3) an anisotropic portion of 70 to 90 percent.

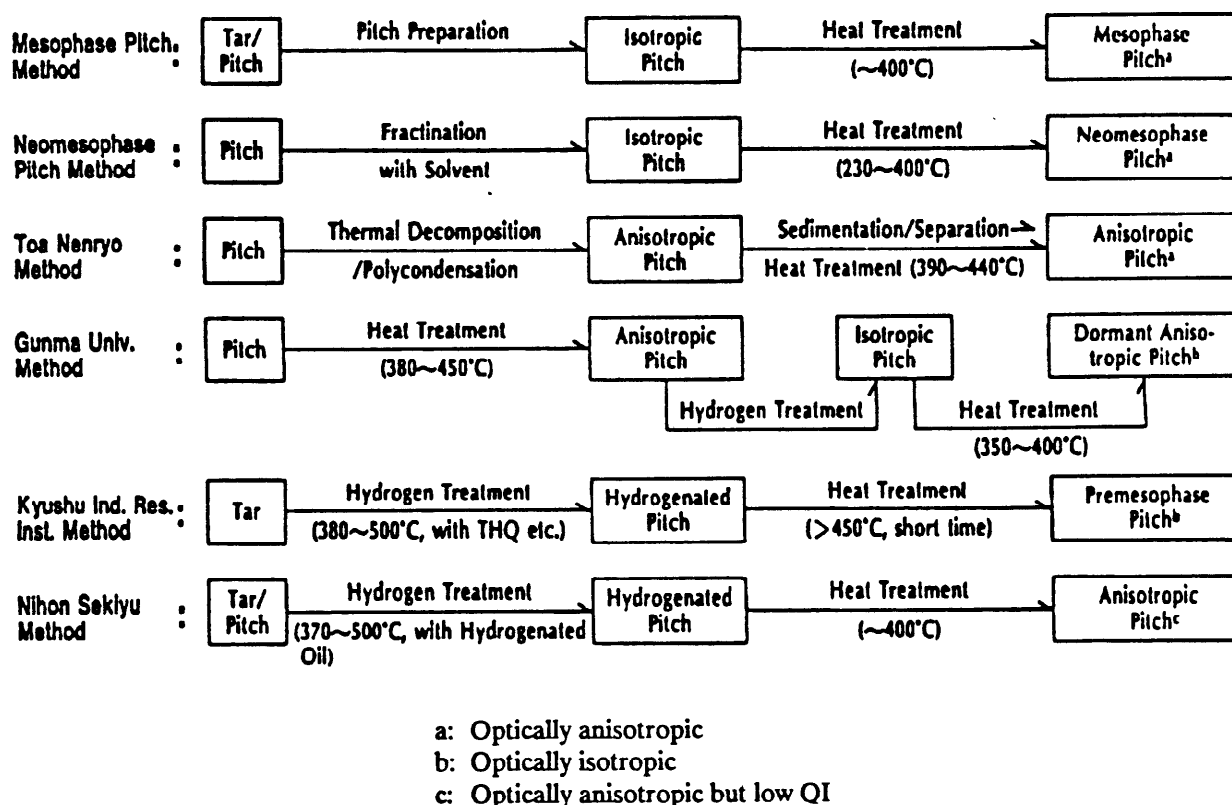


Figure 1. Typical preparation methods for precursor pitch (from Ref 15).

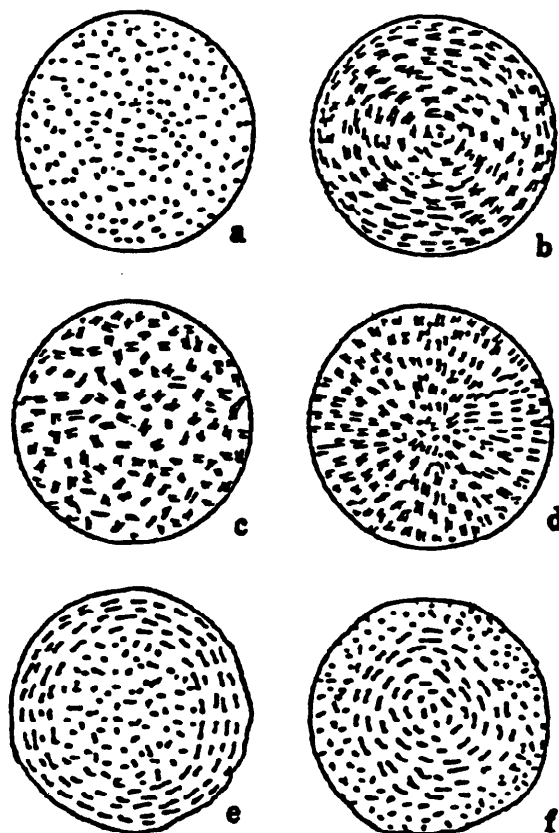


Figure 3. Microstructures of pitch-based carbon fiber cross section (after Ref 15).

The formation of the radial-type cross section (Figure 3d) in the fiber is not preferable due to large thermal shrinkage cracks (Ref 22) that often occur after cooling normal to basal planes of graphite/carbon layers. This type of cross section is presumably produced from a laminar flow of the pitch through the spinneret. Several attempts have been made to change laminar flow to turbulent flow by approaches ranging from changing the shape design of the spinneret, the wettability of the spinneret surface materials, to the addition of a stirring mechanism. The most effective and

the simplest shape of the spinneret is when the orifice has little or no thickness (a "knife edge" shape). Nevertheless, the microstructure of the fiber cross section can be controlled by spinning temperature, drawing rate, spinneret shape, spinneret orifice, and the composition of precursor pitch (Ref 17).

The onion-type cross section is very desirable because crack propagation can occur only along the circumference of the fiber layers according to M. Endo (Ref 23). Thus, the tensile strength of the fiber will be sustained and is less affected by the presence of numerous surface flaws, which are the initiation points of crack formations. This view, however, is not entirely accepted by other scientists. According to Yamada, even in the onion-type cross section, it is impossible to have a perfect cylindrical arrangement of crystallite planes to divert all crack propagations. Preferred orientation and perfect alignment of graphite crystallites in the fiber are believed to be more effective in improving fiber strength.

Design of the fiber cross section by varying the feed pitch composition was also considered. By using a pitch precursor containing two different phases (Ref 17), such as one isotropic low melting and another anisotropic high melting, or isotropic high melting and anisotropic low melting, it is possible to produce a fiber cross section with varying patterns of the desired microstructure. A cross section with the onion layers on the outer circumference (Figure 3e) and the random mosaic microstructure on the fiber core (Figure 3f) has been experimentally attempted. However, the tensile strength of this fiber with the onion outer shell structure (Figure 3f) is not extraordinarily different.

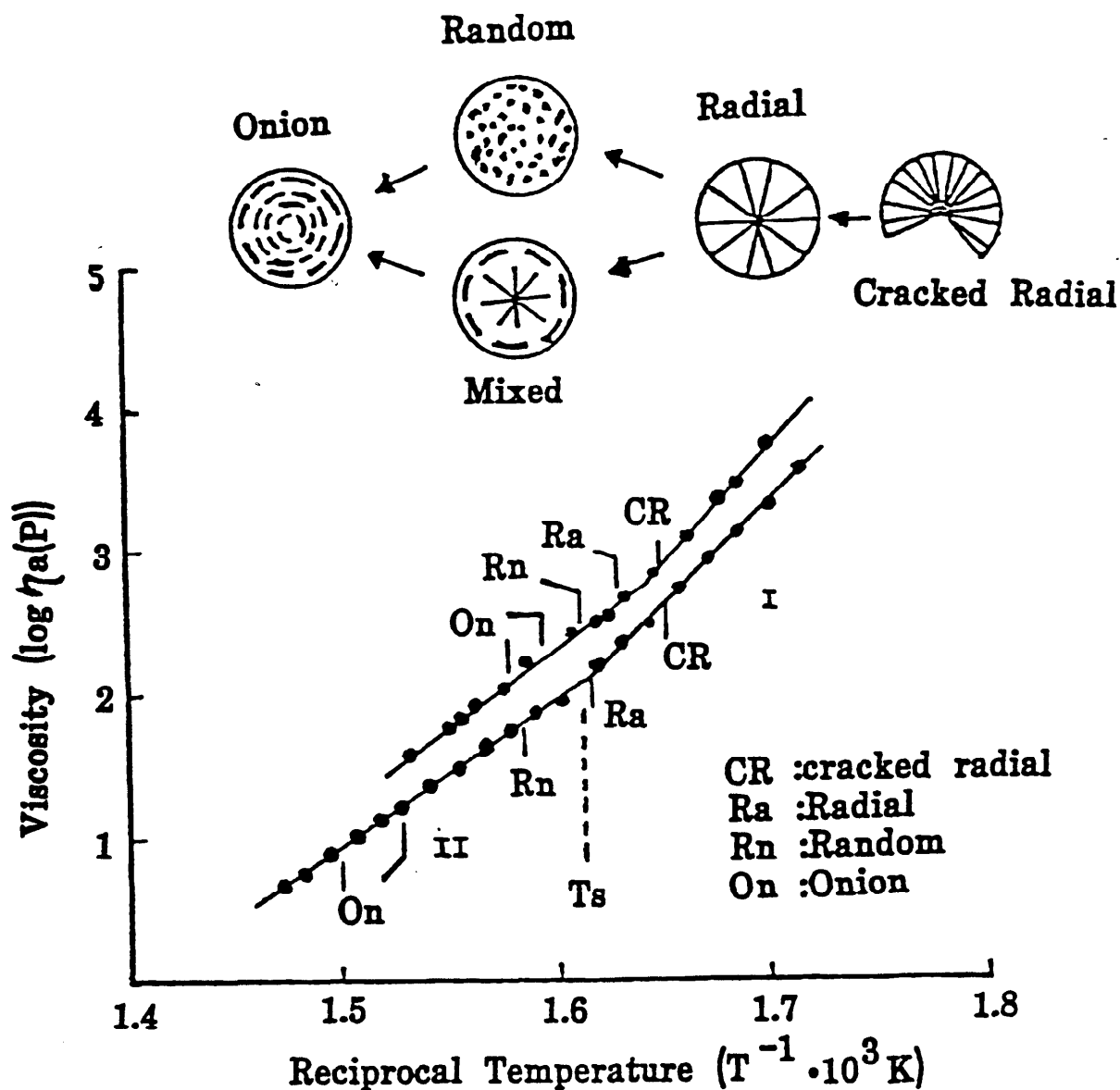
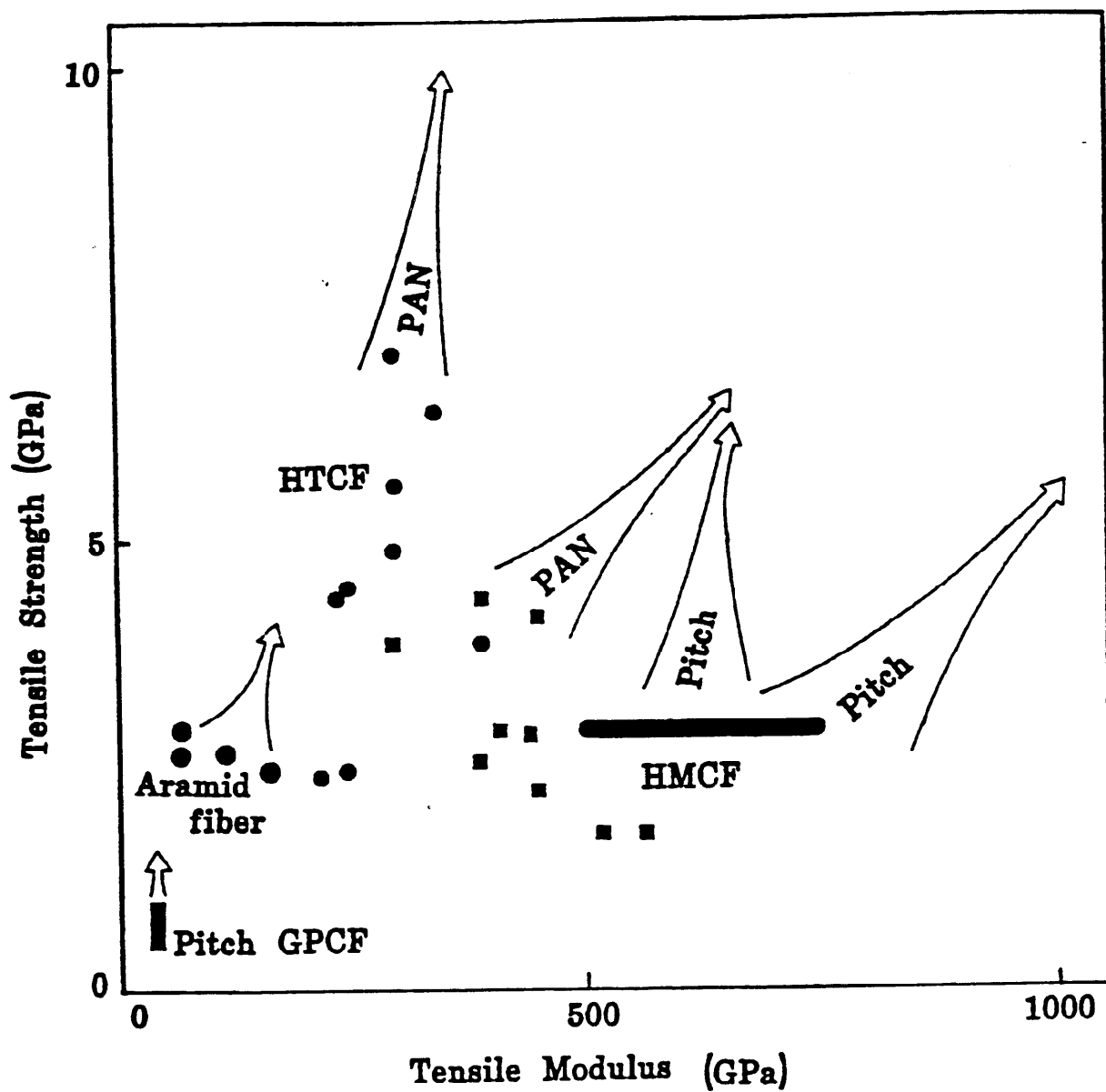


Figure 2. Variation of pitch-based fiber cross sections with softening temperature (from Ref 14).



Square: Pitch-based CF
 Circle: PAN-based CF (small); Aramid fibers (large)
 Arrow: Future trends
 CF: Carbon fiber
 HT: High strength
 HM: High modulus
 GP: General purpose

Figure 4. Mechanical properties of carbon fibers and future trends (after Ref 24).

Several attempts to fabricate fibers with various types of cross sections have been made. By changing the shape of the spinneret and/or by using a stirring device, different cross-sectional patterns, such as elliptic, star, cross, and triangular, with diverse crystallite orientations have been obtained (Ref 4,17). The increase in the circumferences of the odd-shaped ones also increases the number of surface flaws. Consequently, no improvement in material tensile strength was observed. However, the elongated elliptic type of cross section was found to have the best alignment in which two rows of crystallite planes were oriented along the long axis. The tensile strength was also found to improve slightly.

Spinneret shapes other than circular, and with additional stirring devices, are hard to fabricate and may cause difficulties in the processing operation. Moreover, processing parameters such as temperature and draw ratio have to be modified. The alteration in the processing technology may not compensate for the small increment of mechanical strength derived from the non-circular, cross-sectional fibers.

Therefore, the major research efforts in the production of better quality carbon fibers have been in simplifying the preparation method of precursor pitches and finding a more economical processing technology. The immediate concern facing many producers at this time is the large variation of fiber properties from the pilot production line. The mechanical strength of a single filament changes unpredictably from batch to batch and also from segment to segment. This is the major reason that large-scale production of pitch-based fibers has not been fulfilled 10 years after the discovery of the anisotropic mesophase

technology. The cause of this large variation in mechanical strength, which presumably is derived from a large fluctuation in random occurrences of surface flaws, is rather complicated. The problem might come from the inherent nature of the pitch precursor, unforeseen abnormalities in the spinneret and the spinning condition, external as well as internal surface contaminations, and/or stabilization and carbonization processes.

MECHANICAL PROPERTIES

The tensile strength and modulus of typical commercial CF are shown in Figure 4 (Ref 24). According to Figure 4, CF is grouped into three categories: PAN HPCF, p-GPCF, and p-HPCF. The PAN-based fibers are mainly located at the high strength side (3 to 7 GPa) with medium modulus (2 to 300 GPa), while pitch-based HPCF are situated at medium strength (3 GPa) with a wide range of modulus (4 to 800 GPa). It seems that PAN CF are better in tensile strength than pitch HPCF, and the reverse situation exists for tensile modulus. Currently PAN CF M40 made by Toray is commercially available. This fiber has a tensile strength of 4 GPa and a modulus of 400 GPa, which put it in the region bridging the two outstanding features of the PAN and pitch fibers. The fiber currently available with the best tensile stress is Toray T1000 (7 GPa). The highest modulus fiber is pitch CF at 800 GPa. If the current rate of improvement continues, high strengths of 10 GPa for PAN CF and 5 GPa for pitch CF will be attainable within 3 years. The probable directions of future developments for these fibers are indicated by the arrows in the figure.

largest construction using CFRC is a 37-story building in Akasaka, Tokyo. Cost reduction is the largest motivation in the development of CFRC.

Another major expanding application of GPCF is in the field of CF-reinforced plastics. The unique properties of CF in electric conductance and magnetic shielding with moderate strength are the focal points of the application. The commercial use is expected to increase if the cost of GPCF is further reduced by one-half.

The applications of HPCF are different from those of GPCF. Special applications include fiber reinforcements for lightweight, high rigidity composites with zero coefficients of thermal expansion for space use and C/C for aircraft brakes, lightweight missile components, and some durable sporting goods. The number of applications will increase with decreasing cost of HPCF. Thus, increasing utilization of high-performance fibers is expected in the near future.

As for PAN fibers, the current commercial uses are mostly in CF epoxy composites or preregs for aircraft secondary structures. Many CF-reinforced composites with high-temperature resins, such as PEEK and polyimide, have found numerous applications in elevated temperature environments. New formulations of resin have been made to compensate for the low fracture toughness of the CF composites. Some PAN fibers have been substituted for GPCF for essential structural components such as I-beams and tubes. CF with a very high porosity have been made to use as gas absorbants, as water purifiers, or in toxic substances removal. Pre-oxidized CF fabrics are currently available for fireproof clothing and firefighting equipment. Based on the cost trend and the increasing demand

for PAN fibers in recent years, these high-performance fibers may occupy a major role in future structural materials.

FEATURES OF MANUFACTURED PRODUCTS

Producers of PAN-Based Fibers

Toray Industries, Inc. Toray Industries, Inc., is the largest producer of PAN-based carbon fiber with an annual production capacity of 1,500 tons. The corporate research laboratory is well equipped with various research facilities and is actively developing new applications of carbon-fiber-reinforced composites. A wide variety of carbon fibers is commercially available, ranging from a high tensile strength fiber, T1000 (7 GPa), to a high modulus fiber, M50 (500 GPa). An intermediate fiber, such as M46J (with tensile strength and modulus values of 4.2 and 460 GPa, respectively), is also available.

The PAN precursor was produced from the company's own plant. The characteristics and the composition of the precursor polymer are proprietary information. Since the final physical strengths of carbon fibers are strongly dependent on precursor homogeneity, little information was provided concerning the manufacturing process.

The 1985 production capacities for the products of Toray and its licensees (trade name TORAYCA) are as follows:

Toray Industries, Inc., Japan	1,500 tons/yr
SOFICAR S.A., France	300
Amoco Performance Products, Inc., U.S.A.	360
Total	2,160 tons/yr

CF has many superior characteristics uncommon to other materials, such as specific strength, specific modulus, small thermal expansion, excellent fatigue resistance, good corrosion resistance, good damping characteristics, etc. However, one shortcoming other than combustibility is low fracture toughness. The toughness, which is the energy required to fracture material, is about one-tenth of Al alloys. Therefore, improvement in material toughness is urgently needed for the future applications.

To improve the fracture toughness of the CF-reinforced composites (CFRC), a few alternatives and modifications are currently available:

- (1) Improving CF strength by designing new microstructures, or creating an admixture of aramide fibers to form a so-called hybrid composite.
- (2) Enhancing the energy-absorbing mechanism of the composite resin by adding elastomer or thermoplastic polymer and designing a new composition of resin matrix.
- (3) Varying the levels of interfacial adhesion to absorb excessive energy by delamination or fiber pull-out.

The alternative to the last method is to use elastomer as a sizing compound on the surface of CF. The energy-absorbing nature of the elastic interface could prevent fiber delamination and enhance the fracture toughness of the CF-reinforced composites.

PRESENT AND FUTURE APPLICATIONS

The applications of CF to structural components have increased steadily over the past several years. The fibers have been used in applications ranging from the advanced fiber-reinforced composites in the space shuttles and airplane secondary components to biomedical utilization in dental implants.

One of the more significant developments is the application of GPCF in low-cost construction material as a reinforcement (Ref 25 and 26). GPCF traditionally has been used for high-temperature insulating materials. However, in this new application GPCF is expanding into fiber-reinforced cements and concretes. Carbon fiber strengthens the weak tension and poor impact resistance of the conventional portland cement matrix. CF provides:

- Chemical inertness to acid and alkali
- High stability to biodegradation
- Higher tensile strength and modulus compared to concrete
- Good electric and thermal conductances
- High compatibility with cement and mortar

However, the effect of the fiber reinforcement is strongly dependent on fiber strength, formulation, content, and fabrication process, among others. The first and

At the Otake plant and the central research laboratory near Hiroshima I was guided through the acrylic fiber operation. However, the carbon fiber manufacturing line was off limits. The corporate laboratory had many new instruments to facilitate their research efforts, which are concentrated on the improvement of fiber strength, process modification, and the optimum designs for fiber-reinforced composites.

The mechanical properties of Mitsubishi's products (trade name PYROFIL) are as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)
T-1	3.8	250
T-3	5.3	250
MM-1	5.4	315
LM-2	5.9	315
LM-5	5.9	345
HM-2	4.7	420
SM-1	3.9	485

Producers of Pitch-Based Fibers

Kureha Chemical Industry Co., Ltd. This company produces general-purpose, pitch-based short carbon fibers for insulation, felts, and reinforcements of plastic materials. The production of low-cost short fibers was 500 tons last year. This year a new plant will increase the capacity to 1,000 tons. This increasing demand arises from extensive use in short-fiber-reinforced concretes, which have mechanical strengths 10 times that of conventional concretes. The corporate research is aimed at pursuing processing techniques and developing high-performance fibers derived from petroleum pitch. The pitch-based, general-purpose fibers are very cost effective reinforcement materials. There are three

grades of the product: two carbon grades carbonized at 1,000 °C designated as the T-100 series and a graphite grade treated at 2,000°C designated as the T-200 series. The cost is about ¥2,000/kg and is expected to decrease to ¥1,500/kg if sales improve.

Osaka Gas Co., Ltd. Osaka Gas has developed new technology (the so-called Cherry process) for producing carbon fibers from coal tar (Ref 27). In the Cherry process, pitches without any quinoline insoluble components are obtained by continuous heat treatment from crude coal tar, which is a by-product of coal-manufactured gas. The process involves three stages of centrifugal separation of impurities (such as free carbon) at high temperatures. The purified pitches are claimed to have high spinnability and softening point and are used to produce continuous filaments after hydrogenation or to prepare short fibers by rotary gas jets. The products are both high-performance and general-purpose fibers designated as DONACARBO-F and -S. The annual production of short fibers for insulation and felts and low-cost reinforcements is 300 tons, while that of the high-grade fibers is only 10 tons. These short fibers are different than the Kureha Co. fibers, which have curved strands and no circular cross section. Thus, the fiber-reinforced composites will provide better electrical and thermal conductivities because of close contacts among fiber strands. Also, a three-dimensional structure can be readily made.

The major objectives of the corporate developments are to: (1) improve fiber strength by decreasing flaws and pore densities; (2) obtain better control of carbonization temperature; and (3) promote fiber orientation by spinning condition and temperature, nozzle temperature and cooling rate, draw ratio and speed, etc. The project

The products have a wide variety of mechanical characteristics to meet industrial needs. These products are well known and have become commercial standards in the carbon fiber market. The mechanical properties of the TORAYCA products are as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)
T300	3.53	230	1.5
T400H	4.5	250	1.8
T800H	5.59	294	1.9
T1000	7.00	300	--
M30	3.92	294	1.3
M40	2.74	392	0.6
M40J	4.4	392	1.0
M46	2.35	451	0.5
M46J	4.2	451	0.9
M50	2.45	490	0.5

Toho Rayon Co., Ltd. This company is the second largest producer of carbon fibers in the world. Annual production is 1,420 tons, which is second to Toray, but the total production related to carbon fibers, including oxidation resistant and activated fibers, is more than 1,600 tons. The company has a strong tie with BASF (U.S.A.) for technical and marketing agreements. The majority of the fibers produced are exported to the United States, Europe, and southeast Asia. In southeast Asia, Toho products dominate the market.

I visited the Toho Tokyo office and the Mishima laboratory and had friendly discussions with the director, managers, laboratory chief, and engineers. They are very proud of their products and are currently working on the development of new carbon fiber markets, which include many structural components (concrete I-beams, gears, C/C composites, battery shields,

sporting goods, pipes, panels, x-ray beds, and various shaped beams); elastomer-toughened composites; elastomer compounds; and many others. Their central research laboratory was furnished with many up-to-date instruments and research and test facilities. One of the current research efforts on carbon fibers is aimed at enhancing the mechanical strength by increasing the average molecular weight of the PAN polymer (from 10 to 100K) and also by improving the homogeneity of the polymer. Every year there has been improvement in mechanical strength.

The commercial carbon fiber products (trade name BESFIGHT) are not limited to fibers but also include preregs, woven fabrics, chopped fibers, and felts. The mechanical properties of the fibers are as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)
ST-2	4.2	240	1.7
ST-3	4.4	240	1.8
HTA	3.7	240	1.0
HM35	2.7	350	0.8
HM40	2.6	400	0.65
HM45	2.2	450	0.5
IM400	4.2	300	1.4
IM500	4.8	300	1.6
IM600	5.8	300	--

Mitsubishi Rayon Co. This company is the third largest PAN carbon fiber producer in Japan. Although its production at the present time (120 tons) is an order of magnitude less than Toray or Toho, the company is rapidly expanding its production capacity to 500 tons next year. This is based on a growing market with more diversified applications.

particular, the plastic deformation characteristics at high stress are unique. A bundle of fibers (high modulus) can be knotted and twisted without breaking. This fiber property based on the microstructure, composition, or crystallite orientation is extremely interesting. Four grades of carbon fibers (trade name GRANOC) are available. The differences among these fibers are only in the treatment temperatures. The mechanical properties of the fibers are as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)
XN-40	3.23	390	0.83
XN-50	3.23	490	0.66
XN-60	3.23	590	0.55
XN-70	3.3	690	0.49

Toa Nenryo Kogyo K.K. Co. This is the third largest petroleum refining company in Japan. Toa began exploratory research on pitch-based carbon fiber in 1976 and has succeeded in fabricating high-quality pitch-based fibers. Although no commercial product was available at this time, test samples were available in the past year. The advantages of Toa's processing are: (1) efficient mesophase pitch process, (2) high purity and low viscosity precursor pitch, (3) innovative spinning and drawing processes, and (4) advanced and efficient carbonization processes. Since the future success of the carbon fiber industry is dependent on the efficient preparation of raw pitch precursor and a simple processing technique, the research along this direction in my opinion is highly crucial. The mechanical properties of the available carbon fibers are as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)
UHM	3.8	730	0.5
HM	3.2	515	0.6
HT	3.0	270	1.1

ACKNOWLEDGMENTS

The author acknowledges the financial support from the Army Materials Technology Laboratory. The author also appreciates the opportunities to discuss carbon fibers directly with many experts in the field, especially Professor Otani and Dr. Shindo (inventors of anisotropic pitch-based and PAN-based carbon fibers); Dr. Yamada (inventor of the pitch-based carbon fiber hydrogenation process); and Dr. Okuda, Kureha Chemical Co. (coauthor of a carbon fiber book). I am also indebted to many scientists active in carbon fiber research who have provided me with valuable information. Professor Yasuda, Tokyo Institute of Technology, and Mr. Uemura, Toa Nenryo K.K. Co., were particularly helpful in scheduling many of my visits.

REFERENCES

1. B. Kanya, "Corporation strategy of pitch based carbon fiber" (in Japanese), *Nikkei New Materials*, 32-45 (13 July 1987).
2. "Demand, supply and expansion of carbon fiber market" (in Japanese), *New Materials Communication* 1403, 2-3 (30 July 1987).
3. Toho Rayon Co. market research report (April 1988).

manager emphasized that the future outlook of the pitch-based carbon fiber industry is promising due to the low cost of raw materials and the simple processing technology.

The mechanical characteristics of the high-performance fibers are as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)
F-140	1.8	140	1.3
F-500	2.8	500	0.55
F-600	3.0	600	0.5

Kashima Oil Co. (Petroca). This company is relatively small compared to other Japanese carbon fiber producers. Recently it has undertaken a joint venture with the BASF Celion carbon fiber unit (PAN fiber producer) for cooperative research and marketing. This partnership will accelerate cooperation toward the improvement of the process technology. Petroca produces only high-performance carbon fibers. The process involved in manufacturing was stated as being very unique but details were not provided. The quality of the products was claimed to be superior to other fibers. The commercial products are sold in the United States by BASF, and Petroca management was very quiet about the progress the company has made in recent years.

The data provided by Petroca indicated that the products were slightly better in mechanical properties as follows:

Fiber Type	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)
HM50	2.76	490	0.56
HM60	2.94	588	0.5
HM70	2.94	689	0.43

This small oil company was very cautious about our visit because strong market competition from big producers of chemicals and petroleum in the pitch-based carbon fiber business might jeopardize its small share of the market.

Nippon Petrochemical Co., Ltd. Nippon Petrochemical Co., otherwise known as Nippon Oil, has been a pioneer and leader in the Japanese oil industry and is the largest oil company. Nippon Oil's carbon fiber research began 7 years ago in an attempt to convert huge amounts of pitch to high value added products. This research in carbon fiber processing has resulted in successful fabrication of high-grade pitch-based carbon fibers. The company is moving cautiously into carbon fiber production and is building a pilot plant with a capacity of 10 tons at this moment. If the pilot plant is successful, a full-scale production will soon follow.

I visited the corporate central research laboratory at Negishi near Yokohama. A tour of the research laboratories was arranged, but the carbon fiber production line was off limits. The laboratory was well equipped. The properties of their pitch-based carbon fibers are remarkably different from other types of fibers. In

23. T. Hamada, T. Nishida, Y. Sajiki, M. Matsumoto, and M. Endo, *J. Mat. Res.* 2(6), 850 (1987).

24. K. Okuda, "Discussions: Future prospects of ACM" (in Japanese), *Nikkei New Materials*, 84 (13 July 1987).

25. S. Akihama, T. Suenaga, and T. Banno, Mechanical properties of carbon fiber reinforced cement composite and the application to buildings (part 2), Report No. 65 (Kajima Institute of Construction Technology, October 1986).

26. S. Akihama, T. Suenaga, and T. Banno, Mechanical properties of carbon fiber reinforced cement composite and the application to large domes, Report No. 53 (Kajima Institute of Construction Technology, July 1984).

27. Osaka Gas Company, *Sekiyu Gakkaishi* 30(5) (1987).

Sin-Shong Lin, who received a Ph.D. from Kansas University in 1966, has been employed by the Army Materials Technology Laboratory at Watertown, MA, since 1967. Dr. Lin's research interests include chemical thermodynamics, phase diagram, high temperature syntheses, mass spectrometry-atmospheric sampling, and surface analytical techniques (x-ray photon and Auger electron spectroscopies) for material characterizations (of interest are titanium mixed oxides, silicon nitride, gun steel erosion, rubber-elastomer, and carbon fiber). Currently he is active in the fields of surface modification and characterization of carbon fibers. Dr. Lin is a member of the American Chemical Society, American Vacuum Society, Electrochemical Society, Material Research Society, and Carbon Society.

4. S. Otani and A. Oya, "Status report on pitch-based carbon fiber in Japan," in *Proc. Japan-U.S. CCM-III*, Tokyo, Japan (1986); H. Honda, "Carbonaceous mesophase: History and prospects," *Carbon* 26, 139-156 (1988).
5. J.L. White, "Carbon research and development in Japan," *Scientific Bulletin* 9(1), 32 (1984).
6. A. Shindo, Report No. 317 (Osaka Industrial Research Institute, Osaka, Japan, 1961).
7. S. Otani, "On the carbon fiber from the molten pyrolysis products," *Carbon* 3, 31 (1965).
8. Kureha Chem. Co., Japan patents S41-15728, S43-4450, S44-2511.
9. E. Fitzer, editor, *Carbon Fibers and Their Composites* (Springer-Verlag, New York, 1985).
10. J. Delmonte, editor, *Technology of Carbon and Graphite Fiber Composites* (Van Nostrand Reinhold Co., New York, 1984).
11. J.B. Donnet and R.C. Bansal, *International Fiber Science & Technology*, vol 3 (Marcel Dekker Inc., New York, 1985).
12. R.J. Diefendorf, "Carbon/graphite fibers," in *Engineered Materials Handbook*, vol 1, Composites (ASM International, Ohio, 1987), 49-53.
13. J. Bacha, J. Newman, and J. White, editors, "Petroleum derived carbons," *ACS Symposium Series* 303 (1986).
14. K. Yamada, "Production of pitch based carbon fiber," Seminar of the Carbon Society of Japan (1983).
15. K. Okuda, "Pitch based carbon fiber," Second Seminar on Frontier Technology, Shuzenji, Japan, 25-29 May 1987.
16. Toa Nenryo K.K. Co. Japan patent JP S57-88016.
17. K. Yamada, "Structure design of carbon fiber derived from mesophase pitch," paper presented at the 16th Central Region Meeting of the Chemical Society of Japan, 29 November 1985.
18. Y. Yamada, T. Furuta, and M. Shiraishi, "Carbonization and graphitization of anthracene polymer," paper presented at the 14th Semi-Annual Meeting of the Japan Carbon Society, Tokyo, Japan, Dec 1987.
19. Otani et al., "Research related to COPNA resin fibers," paper presented at the 14th Semi-Annual Meeting of the Japan Carbon Society, Tokyo, Japan, Dec 1987.
20. I. Mochida, H. Toshima, and Y. Korai, "Blending mesophase pitch to improve its properties as a precursor for carbon fiber, part I, Blending of PVC pitch into coal tar and petroleum derived mesophase pitches," *Journal of Materials Science* 23, 670 (1988).
21. I. Mochida, H. Toshima, and Y. Korai, "Modification of mesophase pitch by blending," *Journal of Materials Science* 23, 678 (1988).
22. C.B. Ng, G.W. Henderson, M. Buechler, and J.L. White, 16th Biennial Conference on Carbon, San Diego, 1983.

No. of Copies	To	No. of Copies	To
1	Commander, U.S. Army Test and Evaluation Command, Aberdeen Proving Ground, MD 21005	1	National Aeronautics and Space Administration, Langley Research Center, Hampton, VA 23665
1	ATTN: AMSTE-ME	1	ATTN: Mr. J. Buckley, MS 387
1	AMSTE-TD, Mr. H. J. Peters	1	Dr. J. Heyman, MS 231
		1	Mr. R. L. Long, MS 266
1	Commander, U.S. Army Foreign Science and Technology Center, 220 7th Street, N.E., Charlottesville, VA 22901	1	Commander, White Sands Missile Range, Electronic Warfare Laboratory, OMEW, ERADCOM, White Sands, NM 88002
1	ATTN: Military Tech	1	ATTN: Mr. Thomas Reader, AMSEL-WLM-ME
1	Mr. J. Crider		
1	Ms. P. Durrer	1	Department of Energy, Division of Transportation, 20 Massachusetts Avenue, N.W., Washington, DC 20545
1	Mr. P. Greenbaum	1	ATTN: Dr. R. J. Gottschall, ER-131, GTN
1	Chief, Benet Weapons Laboratory, Watervliet, NY 12189	1	Mechanical Properties Data Center, Belfour Stulen Inc., 13917 W. Bay Shore Drive, Traverse City, MI 49684
1	ATTN: AMDAR-LCB-TL		
1	Dr. G. D'Andrea	1	National Institute of Standards and Technology, Washington, DC 20234
1	AMDAR-LCB, Dr. F. Sautter	1	ATTN: E. S. Etz, Bldg. 222, Rm A-121
		1	D. L. Hunston, Bldg. 224, Rm A-209
1	Director, Eustis Directorate, U.S. Army Mobility Research and Development Laboratory, Fort Eustis, VA 23604-5577	1	Dr. D. H. Reneker, Dep. Dir., Ctr for Mat'l's Sci.
1	ATTN: SAVDL-E-MOS (AMCCOM)	1	Dr. Lyle Schwartz
		1	Dr. Stephen Hsu
1	Commander, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS 39180	1	Dr. Allan Draggo
1	ATTN: Research Center Library		
		1	U.S. Bureau of Mines, Mineral Resources Technology, 2401 E. Street, N.W., Washington, DC 20241
1	Project Manager, Munitions Production Base, Modernization and Expansion, Dover, NJ 07801	1	ATTN: Mr. M. A. Schwartz
1	ATTN: AMCPM-PBM-P		
		1	National Institute of Standards and Technology, Gaithersburg, MD 20899
1	Technical Director, Human Engineering Laboratories, Aberdeen Proving Ground, MD 21005-5001	1	ATTN: Dr. S. Wiederhorn
1	ATTN: SLCHD-D, Dr. J. D. Weisz	1	Dr. N. Tighe
1	Chief of Naval Research Arlington, VA 22217	1	National Research Council, National Materials Advisory Board, 2101 Constitution Avenue, Washington, DC 20418
1	ATTN: Code 471	1	ATTN: Dr. K. Zwilsky
1	Dr. A. Diness	1	D. Groves
1	Dr. R. Pohanka	1	J. Lane
1	Naval Research Laboratory, Washington, DC 20375	1	National Science Foundation, Materials Division, 1800 G Street, N.W., Washington, DC 20006
1	ATTN: Code 5830	1	ATTN: Dr. L. Toth
		1	Dr. J. Hurt
1	Headquarters, Naval Air Systems Command, Washington, DC 20360	1	AVCO Corporation, Applied Technology Division, Lowell Industrial Park, Lowell, MA 01887
1	ATTN: Code 5203	1	ATTN: Dr. T. Vasilos
1	Headquarters, Naval Sea Systems Command, 1941 Jefferson Davis Highway, Arlington, VA 22376	1	Case Western Reserve University, Department of Metallurgy, Cleveland, OH 60605
1	ATTN: Code 035	1	ATTN: Prof. A. H. Heuer
1	Headquarters, Naval Electronics Systems Command, Washington, DC 20360	1	Defence Research Establishment Pacific, FMO, Victoria, B.C., VOS 1B0, Canada
1	ATTN: Code 504	1	ATTN: R. D. Barer
1	Commander, Naval Ordnance Station, Louisville, KY 40214	1	Ford Motor Company, Turbine Research Department, 20000 Rotunda Drive, Dearborn, MI 48121
1	ATTN: Code 85	1	ATTN: Mr. A. F. McLean
		1	Mr. J. A. Mangels
1	Commander, Naval Material Industrial Resources Office, Building 537-2, Philadelphia Naval Base, Philadelphia, PA 19112		
1	ATTN: Technical Director	1	Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121
		1	ATTN: Dr. D. Compton, Vice President Research
1	Commander, Naval Weapons Center, China Lake CA 93555		
1	ATTN: Mr. F. Markarian	1	General Electric Company, Research and Development Center, Box 8, Schenectady, NY 12345
		1	ATTN: Dr. R. J. Charles
1	Commander, U.S. Air Force Wright Aeronautical Labs, Wright- Patterson Air Force Base, OH 45433	1	Dr. C. D. Greskovich
1	ATTN: Dr. N. Tallan	1	Dr. S. Prochazka
1	Dr. H. Graham		
1	Dr. R. Ruh	1	Georgia Institute of Technology, EES, Atlanta, GA 30332
1	Aero Propulsion Labs, Mr. R. Marsh	1	ATTN: Mr. J. D. Walton
1	Dr. H. M. Burte		
1	AFWAL/MLLP, Mr. D. Forney	1	GTE Sylvania, Waltham Research Center, 40 Sylvania Road, Waltham, MA 02154
1	AFML/MLLM, Mr. H. L. Geigel	1	ATTN: Dr. W. H. Rhodes
1	AFSC/MLLM, Dr. A. Katz		
		1	Martin Marietta Laboratories, 1450 South Rolling Road, Baltimore, MD 21227
1	Commander, Air Force Armament Center, Eglin Air Force Base, FL 32542	1	ATTN: Dr. J. Venables
1	ATTN: Technical Library		
		1	Massachusetts Institute of Technology, Department of Metallurgy and Materials Science, Cambridge, MA 02139
1	National Aeronautics and Space Administration, Lewis Research Center, 21000 Brookpark Road, Cleveland, OH 44135	1	ATTN: Prof. R. L. Coble
1	ATTN: J. Accurio, USAMRDL	1	Prof. H. K. Bowen
1	Dr. H. B. Probst, MS 49-1	1	Prof. W. D. Kingery
1	Dr. S. Dutta	1	Prof. J. Vander Sande
1	NASA - Scientific and Technical Information Facility, P.O. Box 8757, Baltimore/Washington International Airport, Maryland 21240		

DISTRIBUTION LIST

No. of Copies	To	No. of Copies	To
1	Office of the Under Secretary of Defense for Research and Engineering, The Pentagon, Washington, DC 20301	1	Commander, U.S. Army Missile Command, Redstone Scientific Information Center, Redstone Arsenal, AL 35898-5241
1	ATTN: Mr. J. Persh	1	ATTN: AMSMI-RD-CS-R/Doc
1	Dr. L. Young	1	AMSMI-R, Dr. W. C. McCorkle
1	Mr. K. R. Foster		
	Commander, U.S. Army Laboratory Command, 2800 Powder Mill Road, Adelphi, MD 20783-1145		Commander, U.S. Army Aviation Systems Command, P.O. Box 209, St. Louis, MO 63120-1798
2	ATTN: AMSLC-IM-TL	1	ATTN: AMSAV-NS, Mr. M. L. Bauccio
1	AMSLC-TD	1	Technical Library
1	AMSLC-TD-A		
1	AMSLC-PA		Commander, U.S. Army Natick Research, Development, and Engineering Center, Natick, MA 01760
1	AMSLC-TP	1	ATTN: Technical Library
	Commander, Defense Technical Information Center, Cameron Station, Building 5, 5010 Duke Street, Alexandria, VA 22304-6145	1	Dr. J. A. Sousa
2	ATTN: DTIC-FDAC	1	Dr. R. J. Byrne
1	National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161	1	Dr. R. Lewis
	Director, Defense Advanced Research Projects Agency, 1400 Wilson Boulevard, Arlington, VA 22209		Commander, U.S. Army Satellite Communications Agency, Fort Monmouth, NJ 07703
1	ATTN: Dr. P. Parrish	1	ATTN: Technical Document Center
1	Dr. B. Wilcox		Commander, U.S. Army Science and Technology Center Far East Office, APO San Francisco, CA 96328
1	Dr. K. Hardmann-Rhyne	1	ATTN: Terry L. McAfee
	Battelle Columbus Laboratories, Metals and Ceramics Information Center, 505 King Avenue, Columbus, OH 43201		Commander, U.S. Army Communications and Electronics Command, Fort Monmouth, NJ 07703
1	ATTN: Mr. W. Duckworth	1	ATTN: AMSEL-TDD, Mr. T. A. Pfeiffer, Technical Dir.
1	Dr. D. Niesz		Director, Electronic Technology and Devices Lab, Fort Monmouth, NJ 07703
	Department of the Army, Office of the Assistant Secretary of the Army (RDA), Washington, DC 20310	1	ATTN: DELET-D, Dr. C. G. Thornton
1	ATTN: Dr. J. G. Prather, Dep for Sci & Tech		Commander, U.S. Army Tank-Automotive Command, Warren, MI 48397-5000
1	Dr. J. R. Sculley, SARD	1	ATTN: Dr. W. Bryzik
	Deputy Chief of Staff, Research, Development, and Acquisition, Headquarters, Department of the Army, Washington, DC 20310	1	D. Rose
1	ATTN: DAMA-ZE, Mr. C. M. Church	1	AMSTA-RKA
	Commander, U.S. Army Research and Development Office, Chief Research and Development, Washington, DC 20315	1	AMSTA-UL, Technical Library
1	ATTN: Physical and Engineering Sciences Division	1	AMSTA-R
	Commander, Army Research Office, P.O. Box 12211, Research Triangle Park, NC 27709-2211	1	AMSTA-NS, Dr. H. H. Dobbs
1	ATTN: Information Processing Office		Commander, U.S. Army Armament, Munitions and Chemical Command, Dover, NJ 07801
1	Dr. J. Hurt	1	ATTN: Mr. J. Lannon
1	Dr. A. Crowson	1	Mr. H. E. Peibly, Jr., PLASTEC, Director
1	Dr. R. Reeber	1	Technical Library
1	Dr. R. Shaw	1	Dr. T. Davidson
	Commander, U.S. Army Materiel Command, 5001 Eisenhower Avenue, Alexandria, VA 22333	1	Dr. B. Ebihara
1	ATTN: AMCQA-EQ, Mr. H. L. Light		Commander, U.S. Army Armament, Munitions and Chemical Command, Rock Island, IL 61299
1	AMCQA, Mr. S. J. Lorber	1	ATTN: Technical Library
	Commander, U.S. Army Electronics Research and Development Command, Fort Monmouth, NJ 07703-5000		Commander, Aberdeen Proving Ground, MD 21005
1	ATTN: AMDET-ES, Dr. A. Tauber	1	ATTN: AMDAR-CLB-PS, Mr. J. Vervier
	Director, Electronics Warfare Laboratory, Fort Monmouth, NJ 07703		U.S. Army Corps of Engineers, Construction Engineering Research Lab, P.O. Box 4005, Champaign, IL 61820
1	ATTN: AMDEW-D, Mr. M. Adler	1	ATTN: Dr. Robert Quattrone
	Commander, U.S. Army Materiel Systems Analysis Activity, Aberdeen Proving Ground, MD 21005		Commander, U.S. Army Belvoir RD&E Center, Fort Belvoir, VA 22060-5606
1	ATTN: AMXSY-MP, H. Cohen	1	ATTN: STRBE-FS, Mr. W. McGovern, Fuel & Wtr Sup Div
	Commander, U.S. Army Night Vision Electro-Optics Laboratory, Fort Belvoir, VA 22060	1	AMDME-V, Mr. E. York
1	ATTN: DELNV-S, Mr. P. Travesky	1	STRBE-ZTS, Dr. K. H. Steinbach, Office of the Chief Scientist
1	DELNV-L-D, Dr. R. Buser	1	AMDME-ZT, Mr. T. W. Lovelace, Tech Dir
1	DELNV-D, Dr. L. Cameron	1	Mr. M. Lepera
	Commander, Harry Diamond Laboratories, 2800 Powder Mill Road, Adelphi, MD 20783		Director, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD 21005
1	ATTN: Technical Information Office	1	ATTN: SLCBR-BLT, Dr. A. M. Dietrich
1	SLCHD-RAE	1	SLCBB-BLF, Dr. A. Niller
	Director, U.S. Army Research & Technology Labs, Ames Research Center, Moffet Field, CA 94035		Commander, Rock Island Arsenal, Rock Island, IL 61299
1	ATTN: DAVDL-D, Dr. R. Carlson	1	ATTN: SARRI-EN
1	DAVDL-AL-D, Dr. I. C. Statler, MS215-1, Aeromechanics Laboratory		Director, U.S. Army Industrial Base Engineering Activity, Rock Island, IL 61299
		1	ATTN: AMXIB-MT, Mr. G. B. Ney
			Chemical Research and Development Center, Aberdeen Proving Ground, MD 21010
		1	ATTN: AMSMC-CLD(A), Dr. B. Richardson

No. of Copies	To
1	Materials Research Laboratories, P.O. Box 50, Ascot Vale, VIC 3032, Australia ATTN: Dr. C. W. Weaver
1	Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 64110 ATTN: Mr. G. W. Gross, Head, Physics Station
1	Pennsylvania State University, Materials Research Laboratory, Materials Science Department, University Park, PA 16802 ATTN: Prof. R. Roy
1	Prof. R. E. Newnham
1	Prof. R. E. Tressler
1	Dr. C. Pantano
1	Mr. C. O. Ruud
1	State University of New York at Albany, Department of Physics, Albany, NY 12222 ATTN: Prof. W. A. Lanford
1	State University of New York at Stony Brook, Department of Materials Science, Long Island, NY 11790 ATTN: Prof. F. F. Y. Wang
1	Stanford Research International, 333 Ravenswood Avenue, Menlo Park, CA 94025d ATTN: Dr. P. Jorgensen
1	Dr. D. Rowcliffe
1	United Technologies Research Center, East Hartford, CT 06108 ATTN: Dr. J. Brennan
1	Dr. K. Prewo
1	University of California, Lawrence Livermore Laboratory, P.O. Box 808, Livermore, CA 94550 ATTN: Mr. R. Landingham
1	Dr. C. F. Cline
1	Dr. J. Birch Holt
1	University of Florida, Department of Materials Science and Engineering, Gainesville, FL 32611 ATTN: Dr. L. Hench
1	University of Washington, Ceramic Engineering Division, FB-10, Seattle, WA 98195 ATTN: Prof. R. Bradt
1	Westinghouse Electric Corporation, Research Laboratories, Pittsburgh, PA 15235 ATTN: Dr. R. J. Bratton
1	Battelle Pacific Northwest Lab, NDT Section, Richland, WA 99353 ATTN: Mr. A. Birks, Associate Manager
1	Rensselaer Polytechnic Institute, Department of Materials Engineering, Troy, NY 12181 ATTN: R. J. Diefendorf
1	Oak Ridge National Laboratory, P.O. Box X Oak Ridge, TN 37830 ATTN: P. F. Becher
1	V. J. Tennery
1	R. Johnson
1	Sandia Laboratories, Albuquerque, NM 87185 ATTN: Dr. F. Gerstle, Div 5814
1	The John Hopkins University, Department of Civil Engineering/ Materials Science and Engineering, Baltimore, MD 28218 ATTN: Dr. R. E. Green, Jr.
1	Director, Office of Science and Technology Policy, Old Executive Office Building, Washington, DC 20223

No. of Copies	To
1	Subcommittee on Science, 2319 Rayburn House Office Building, Washington, DC 20515 ATTN: Mr. P. C. Maxwell
1	Aerospace Corporation, Materials Science Laboratory, 2350 East El Segundo Boulevard, El Segundo, CA 90245 ATTN: Dr. L. R. McCreight
1	IBM Corporation, Thomas B. Watson Research Center, Yorktown Heights, NY 10598 ATTN: Dr. G. Onoda
1	Corning Glass Works, Research and Development Division, Corning, NY 14830 ATTN: Dr. W. R. Prindle
1	3M Company, New Products Department, 219-01-01, 3M Center, St. Paul, MN 55144 ATTN: R. E. Richards
1	Technology Strategies, Inc., 10722 Shingle Oak Ct., Burke, VA 22015 ATTN: Dr. E. C. Van Reuth
1	Rutgers University, Center for Ceramics, Rm A274, P.O. Box 909, Piscataway, NJ 08854 ATTN: Prof. J. B. Wachtman, Jr., Director
1	Syracuse University, 304 Administration Building, Syracuse, NY 13210 ATTN: Dr. V. Weiss
1	Lehigh University, Materials Research Center #32, Bethlehem, PA 18015 ATTN: Dr. D. M. Smyth
1	Alfred University, New York State College of Ceramics, Alfred, NY 14802 ATTN: Dr. R. L. Snyder
1	Alfred University, Center for Advanced Ceramic Technology, Alfred, NY 14802 ATTN: R. M. Spriggs
1	University of California, Center for Advanced Materials, 058, Hildebrand Hall, Berkeley, CA 94720 ATTN: Prof. G. Somorjai
1	Boeing Aerospace Company, 11029 Southeast 291, Auburn, MA 98002 ATTN: W. E. Strobelt
1	University of California, Materials Science and Mineral Engineering, Heart Mining Building, Rm 284, Berkeley, CA 94720 ATTN: Prof. G. Thomas
2	Director, U.S. Army Materials Technology Laboratory, Watertown, MA 02172-0001 ATTN: SLCMT-TML
1	Author